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AD-A221 392

REPORT DOCUMENTATION PAGE

DTIC
ELECTE
MAY 11 1990
S B D

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
TR 90001	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Diamond Materials, Inc.		Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
2820 East College Avenue State College, PA 16801	Code 1114 800 N. Quincy Street Arlington, VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
Office of Naval Research		

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
800 N. Quincy Street Arlington, VA 22217-5000	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO
		4000047		sbi 01

11. TITLE (Include Security Classification)

Synthesis of Large Area, Monocrystalline TiC as a Substrate for Heteroepitaxial Growth of β-SiC

12. PERSONAL AUTHOR(S)
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13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 89/9/7 TO 90/5/7	1990, May 7	19

16. SUPPLEMENTARY NOTATION

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Beta silicon carbide, silicon, heteroepitaxy, titanium carbide

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Work on this program has focused on achieving the heteropitaxial growth of monocrystalline β-SiC on silicon substrates. DMI has finishing de-bugging its upgraded β-SiC CVD reactor. Experiments were performed to determine the optimal etching treatment for silicon substrates to prepare them for β-SiC CVD. Etching experiments using pure H_2 and 1-5 % HCl/H_2 indicated that mild etching of the silicon surface only served to decorate crystallographic defects left behind by the chem-mechanical polishing of the Si wafer. A vigorous etch by 5% HCl/H_2 at 1300°C for 10 minutes was sufficient to remove several microns of the silicon, exposing a reasonably flat and smooth Si surface suitable for β-SiC heteroepitaxial growth. DMI believes it has grown heteroepitaxial β-SiC on Si from 1.9% methyltrichlorosilane (MTS) diluted in H_2 at 1300 - 1400°C for five minutes. To finish the program, DMI will work to grow a ≈30 μm thick, freestanding β-SiC single crystal and will perform a chlorinated oxidation on the β-SiC to getter crystallographic defects from its surface. TiC will be then be deposited onto the β-SiC single crystal by CVD.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	UNCLASSIFIED

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

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90 05 11 081

TECHNICAL REPORT

Synthesis of Large Area, Monocrystalline TiC as a Substrate
for Heteroepitaxial Growth of β-SiC

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May 7, 1990

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Contract No. N00014-89-C-0208

TECHNICAL REPORT

Synthesis of Large Area, Monocrystalline TiC as a Substrate
for Heteroepitaxial Growth of β-SiC

1.   INTRODUCTION

The purpose of this program is to demonstrate a novel process for synthesis of large area TiC single crystals. This SBIR program directly supports DoD efforts to develop monocrystalline β-SiC as a semiconductor material. β-SiC semiconductor devices offer the promise of one day replacing vacuum tubes as the source of microwaves for radar and communications. Because the cubic ("beta") polymorph of SiC is unstable at the sublimation temperature of SiC, the only methods demonstrated to produce large, single crystals of β-SiC have been heteroepitaxial growth by chemical vapor deposition (CVD). Monocrystalline Si, α-SiC, and TiC are all viable substrates for the heteroepitaxial growth of monocrystalline β-SiC. Of the three substrates, only TiC has been demonstrated to produce β-SiC films free of stacking faults, misfit dislocations, inversion domain boundaries, and *double positioning boundaries*. Additionally, TiC offers the advantage of being a good electrical conductor, exhibiting excellent ohmic contact to n-type β-SiC with low contact resistance. Therefore, β-SiC single crystal films grown on TiC substrates would be ideally suited for the fabrication of vertical FETs. Vertical FETs, such as the permeable base transistor (PBT), have achieved extremely high-power/high-frequency operation when fabricated in Si and GaAs.

CVD of monocrystalline β-SiC films on TiC has been limited by the unavailability of large area, TiC single crystals. TiC has numerous materials properties which make it difficult to grow as a large, monocrystalline boule by traditional crystal growing methods such as the float zone process. The economic viability of β-SiC semiconductors depends on the production of large-area TiC single crystals. Conventional TiC crystal growing methods (such as the float zone process) seem unlikely to synthesize large diameter, (i.e., up to 10 cm), monocrystalline boules of pure TiC free of pores, pinholes, and subgrain boundaries.

In this SBIR program, Diamond Materials, Inc. (DMI) is being funded to pursue a novel approach to the synthesis of large-area TiC single crystals. A summary of DMI's proposed procedure is as follows:

1. Heteroepitaxial β-SiC will be grown by CVD on silicon wafers. The β-SiC will be grown to a thickness in excess of ≈30 μm.

2. The silicon substrate will be selectively removed from the β-SiC film.

3. DMI will attempt to getter crystallographic defects from the outer ≈ 1 μm portion of the β-SiC single crystal by means of chlorinated oxidation. DMI will determine whether or not chlorinated oxidation can reduce the areal density of crystallographic defects on the β-SiC single crystal.

4. The gettered β-SiC single crystal surface will then be used as a substrate for the heteroepitaxial growth of TiC by chemical vapor deposition. The excellent lattice match of β-SiC to TiC should enable CVD of monocrystalline TiC.

2.   ACCOMPLISHMENTS TO DATE

Diamond Materials, Inc. has focused its efforts on achieving the heteroepitaxial growth of monocrystalline β-SiC on silicon wafers. In summary, DMI has: (a) de-bugged its recently upgraded β-SiC CVD reactor, (b) learned how to etch silicon with HCl/H₂ mixtures to prepare the surface for β-SiC heteroepitaxy, (c) started experiments on CVD of β-SiC onto silicon using the source gas methyltrichlorosilane (MTS). DMI's next step is to grow a thick, monocrystalline β-SiC film on silicon and complete tasks 2, 3 and 4 as described in Section 1 above.

2.1   De-bug the β-SiC Reactor

As was described in the Progress Report (Sept. 7, 1989), DMI's β-SiC CVD reactor underwent extensive engineering modifications and additions, including: (a) a quick response gas handling system, (b) a completely redesigned "bell jar" assembly utilizing standard sized fused silica tubes, (c) a redesigned susceptor assembly, (d) an increase in the number of mass flow controllers (MFCs) to ten, and (e) a heating system which maintains the MTS bubbler, the MTS MFC and the MTS stainless steel tubing at a constant temperature of 50°C to mitigate condensation of MTS downstream from the bubbler. (The boiling point of MTS is 66°C).

A major accomplishment to date has been mastery of the new gas flow logic. Several days were spent determining the necessary sequence of pneumatic valve positions and MFC actuation in order to ensure the proper flow. The MTS valving was especially complex since the special MTS bubbler (purchased from ATM, Inc.) is versatile, enabling direct flow of MTS impelled by MTS vapor pressure, or assisted flow of MTS using a H_2 carrier gas. After experimentation, it was decided to flow pure MTS through the MFC without any assistance from a carrier gas in order to maximize MTS flow accuracy and precision.

Minor problems were encountered and solved, such as replacement of defective MFC cables, cracked silica bell jars, and depletion of MTS supply. Since the β-SiC needed for this Phase I program does not have to be of semiconductor grade purity, DMI is employing reagent-grade MTS which is 98% pure packed in Ar. Although our β-SiC films are undoubtedly doped with residual nitrogen, the reagent-grade MTS is available in the necessary quanities without the weeks of lead time needed for a vendor to perform MTS purification.

2.2   Approach to β-SiC Heteroepitaxy on Si

Based on conversations with experts, and by reading the literature, DMI felt that the optimal process for CVD of heteroepitaxial β-SiC on Si should be isothermal, or as close to isothermal as possible. The original procedure described by J. A. Powell and co-workers called for a two-step procedure where an initial thermal excursion is performed to etch the silicon in HCl/H_2, and a subsequent excursion is performed to first carburize and then deposit β-SiC from hydrocarbon + silane mixtures. The reason for the cool to room temperature after the HCl etch was probably to ensure complete purging of residual HCl from the CVD reactor before starting the β-SiC nucleation and growth step.

MTS, (CH_3SiCl_3), is a source gas which decomposes as:

$$CH_3SiCl_{3(v)} = SiC_{(s)} + 3HCl_{(v)}$$
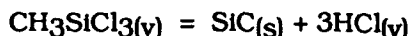
Hence, deposition of β-SiC from MTS includes a concurrent HCl etching phenomenon which helps prevent the co-deposition of elemental silicon, graphite and α-SiC. DMI decided to deposit β-SiC immediately following the HCl etch step without cooling the substrate to room temperature.

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The use of MTS should also make it unnecessary to carburize the silicon surface in order to nucleate a monocrystalline β-SiC layer. The carburization step was shown to generate defects in heteroepitaxial β-SiC in research performed by Molnar and Shirey of Naval Reseach Lab, (poster F8.7 presented at the Fall 1989 Materials Reseach Society meeting, "SEM Observation of Growth and Defect Formation on Heteroepitaxially Grown SiC on (100) Silicon.") Molnar and Shirey noted that a localized excess of reactive carbon at the silicon surface (i.e., during carburization) prompts outdiffusion of silicon from the near-surface region, creating "potholes" beneath the β-SiC film which exacerbate β-SiC film stress. Flowing a hydrocarbon over a silicon surface $\geq 1300°C$ without also flowing a silicon source (e.g., silane) invites excessive outdiffusion of silicon from the substrate.

As demonstrated by Nishino and Saraie, ("Epitaxial Growth of 3C-SiC on a Si Substrate Using Methyltrichlorosilane," in Amorphous and Crystalline SiC, ed. by Harris and Yang, Springer-Verlag (1989) p. 45), carburization with a hydrocarbon is unnecessary to nucleate β-SiC when using MTS. Nishino and Saraie directly nucleated and grew heteroepitaxial β-SiC using 1 sccm of MTS plus 1 SLM of H_2 at 1300°C, (i.e., 0.1% MTS/H_2). Prior to MTS flow, they performed a separate temperature excursion for HCl/H_2 etching, which DMI believes is unnecessary.

DMI's goal is to develop a CVD procedure for β-SiC growth on Si composed of: (1) pump down to ultimate vacuum, (2) backfill with hydrogen to 250 torr and maintain that pressure for all subsequent steps, (3) heat up in H_2 to a fixed temperature (4) add HCl/H_2 to etch the silicon surface, (5) immediately switch off the HCl and add MTS/H_2 to nucleate and grow β-SiC, (6) turn off the MTS/H_2 and cool to room temperature in argon.

2.3   Hydrogen Etching Experiments

At the beginning of this program, DMI believed that the purpose of the HCl/H_2 etch step was simply to remove native oxide from the silicon crystal. Hence, an initial goal was to determine a heat up and etch sequence which would produce a flat, pinhole free silicon surface which would be free of native oxide immediately before commencing MTS flow.

Heat up experiments were performed in H_2. It was concluded that heat up in H_2 is preferrable to heat up in Ar because of the significantly higher thermal conductivity of H_2. Switching from Ar to H_2 would make it difficult to maintain substrate temperature continuity. Since the substrate is inductively heated, a sudden switch from

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Ar to H_2 would cause the substrate temperature to plummet faster that the rf power supply could respond.

All experiments performed in the ß-SiC reactor to date share a number of similarities. The total pressure is fixed at 250 torr and is maintained by a special high pressure throttle valve working in concert with a capacitance manometer. The wafers were cleaned according to the standard RCA procedure before being inserted into the reactor. It was observed that pure H_2 had the ability to etch the silicon surface. A series of runs were performed to determine the temperature to which silicon would be heated without sufferingH_2 etching. This temperature was determined to be 1000°C.

2.4   HCl/H_2 Etching Experiments

After H_2 etching was investigated, DMI began performing HCl/H_2 etching experiments. Again, DMI believed that the reason why all published recipes for ß-SiC heteroepitaxy included a preliminary etch was to remove native oxide. HCl/H_2 etching experiments were performed at temperatures between 1000 and 1300°C and at concentrations between 1 and 5% HCl diluted in H_2. It was observed that pitting of the silicon surface was almost always observed when flowing HCl except when the temperature was below 900°C.

After close microscopic examination of the etch pits, and re-examination of the published HCl etch recipes, it became clear that DMI had *misinterpreted* the true reason for the HCl etch step. All of DMI's H_2 and HCl etch experiments were simply decorating crystalline defects present in the surface of silicon wafers. The chem-mechanical methods used to polish all semiconductor-grade silicon leaves the near-surface region of the silicon crystal riddled with stacking faults and other point and line defects. Defect gettering from the silicon surface is typically accomplished by HCl/O_2 oxidation. DMI's mild HCl etch experiments were simply identifying the presence of crystalline defects near the wafer surface. DMI realized that the *real* motivation for the HCl etch prior to ß-SiC growth is to etch away *several microns* of silicon to expose fresh defect-free silicon. Because the contribution of the hydrogen etch to the total HCl/H_2 etch was minor, the pure H_2 etch portion of the procedure was eliminated.

DMI obtained a desirable result by increasing the aggressiveness of the HCl etch procedure. In run 44, 5 sccm of HCl plus 95 sccm of H_2 were run for 5 minutes at 1300°C, with cool down in argon. The result was the formation of a layer of silicon which had almost completely detached from the silicon surface. The silicon layer was several microns thick, and was bowed upward, still attached to the substrate at the center. In

run 46, the process conditions of run 44 (5% HCl/H$_2$ at 1300°C) were repeated for a longer time, 10 minutes, and resulted in complete removal of the defective layer of silicon. Figure 1 is a SEM micrograph of the flat bottom hole cut into the silicon wafer during run 46. The hole is ≈5 μm deep and has a rather smooth texture at its bottom. It is apparaent that the HCl had to remove the outer 5 μm of silicon to reach a silicon region which etches at a uniform rate. Uniform etching over the area of the surface indicates a lack of point defects left behind in the silicon by the chem-mechanical polishing step.

The etch procedure developed in run 46 was then instituted for all subsequent MTS runs. An etch temperature of 1300°C was desirable since CVD of of heteroepitaxial ß-SiC should occur at a similar temperature.

2.5   ß-SiC Growth Experiments

A listing of the MTS growth experiments performed so far appears in Table 1. Each MTS growth experiment immediately followed the 5% HCl/H$_2$ etch procedure defined by run 46.

Table 1: ß-SiC Growth Experiments.

Run	Flow (sccm)		% MTS	Duration (min.)	Temp. (°C)
	Hydrogen	MTS			
49	200	1	0.50	5	1300
52	300	1	0.33	5	1300
53	250	1	0.40	5	1300
59	300	3	1.0	5	1300
60	250	4.75	1.9	5	1300
63	250	4.75	1.9	5	1300-1400

SEM micrographs of the samples described in Table 1 appear as Figures 2 - 8. Comparing the figures, it is apparent that the thickness of the films is proportional to the MTS percentage. The figures also indicate the evolution of ß-SiC film microstructure. Figure 7B shows the edge view of afilm. The ß-SiC films grow in two stages. The initial stage is island growth of oriented ß-SiC crystals. When seen in plan
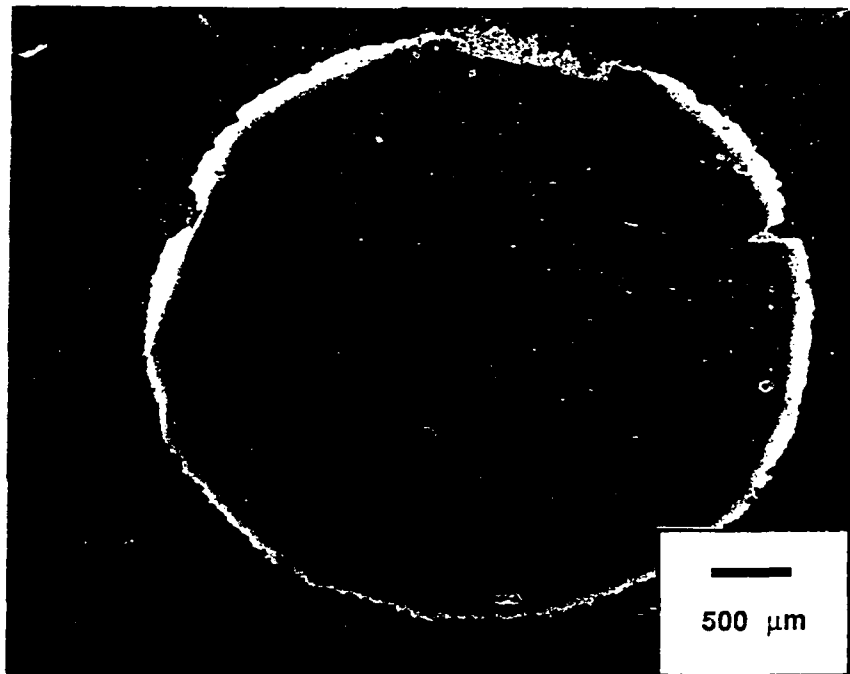
FIGURE 1. Run 46. SEM micrograph of flat-bottom crater in silicon
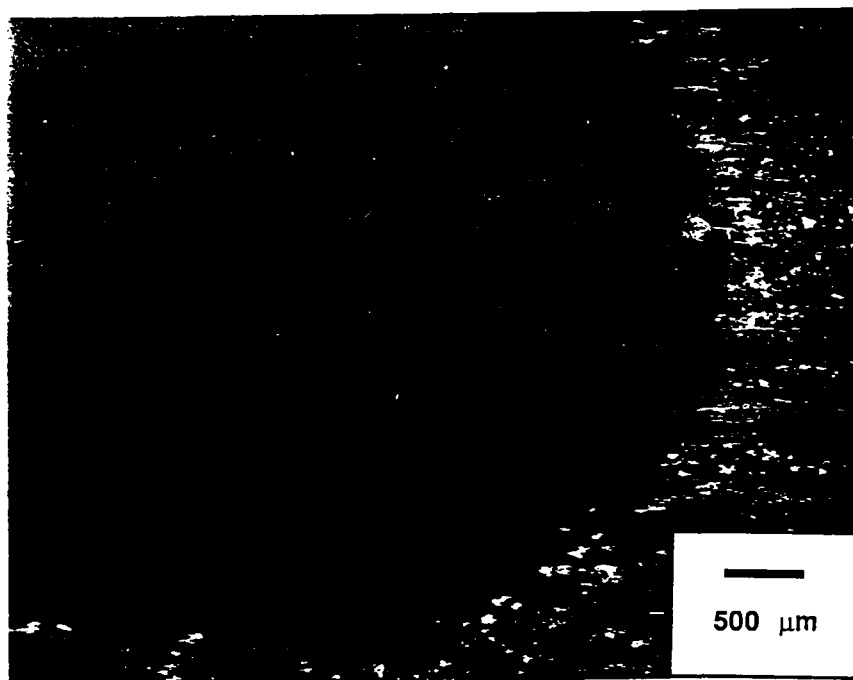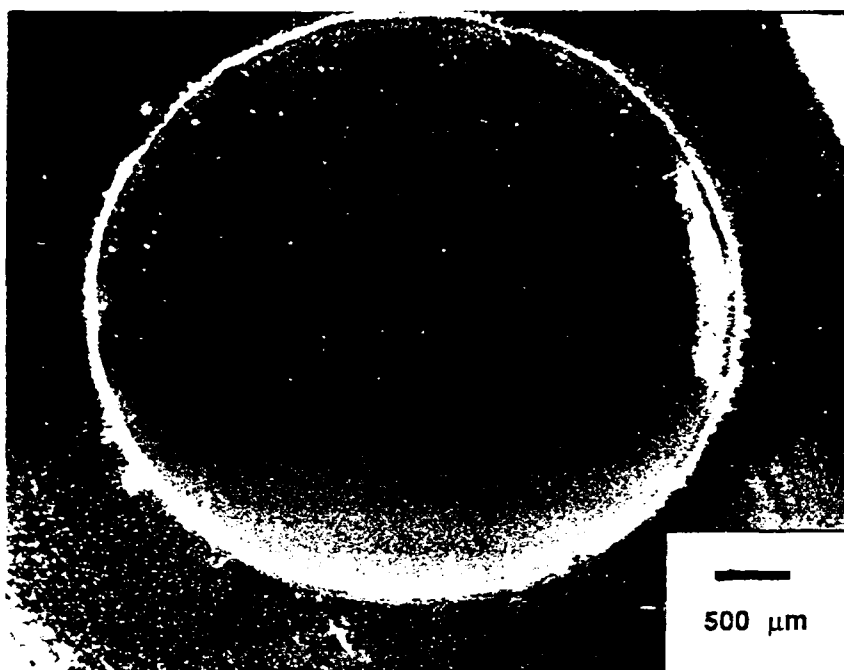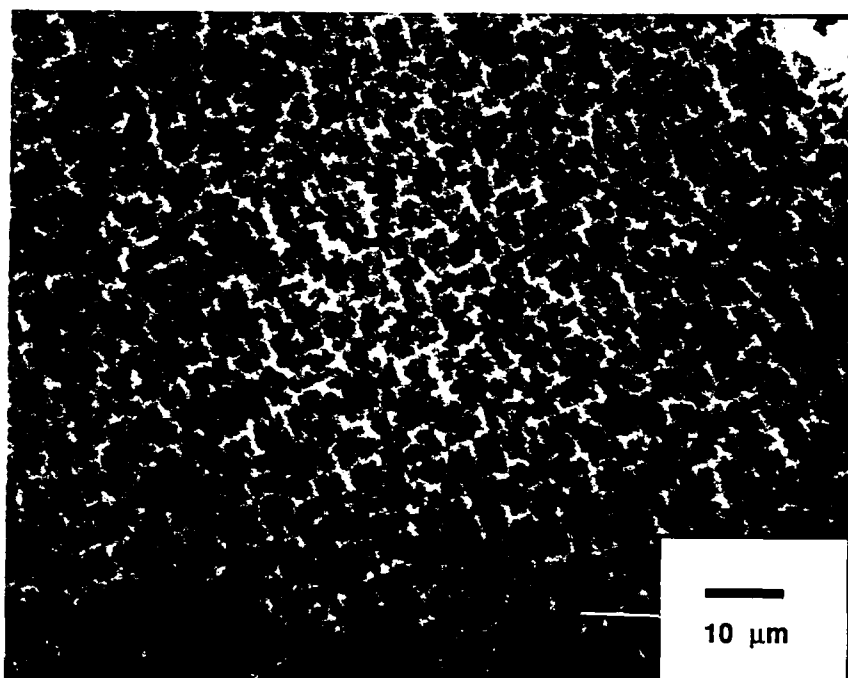created by 10 minutes of 5% HCl/H2 etching at 1300°C.

FIGURE 2. Run 49. SEM micrograph of film grown from 0.50%
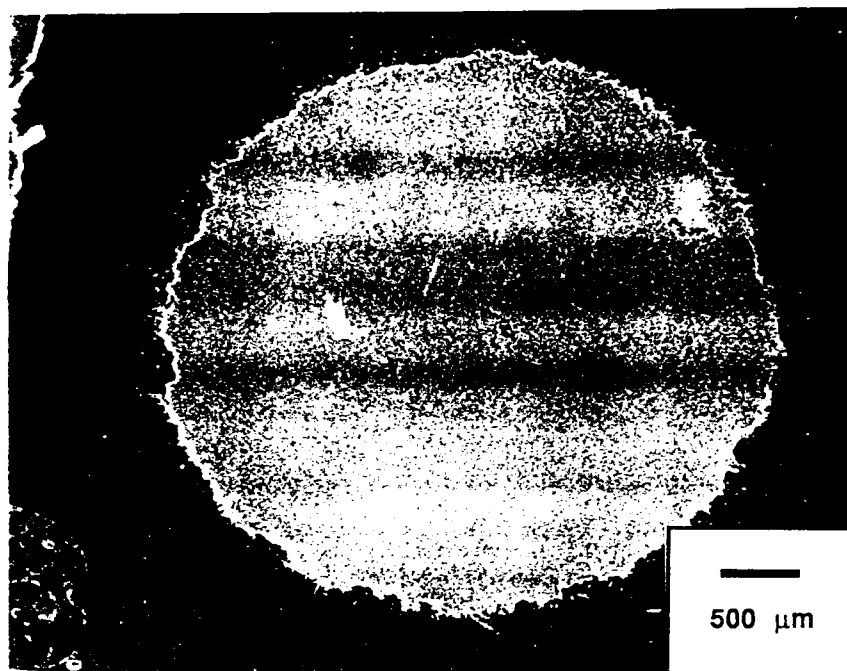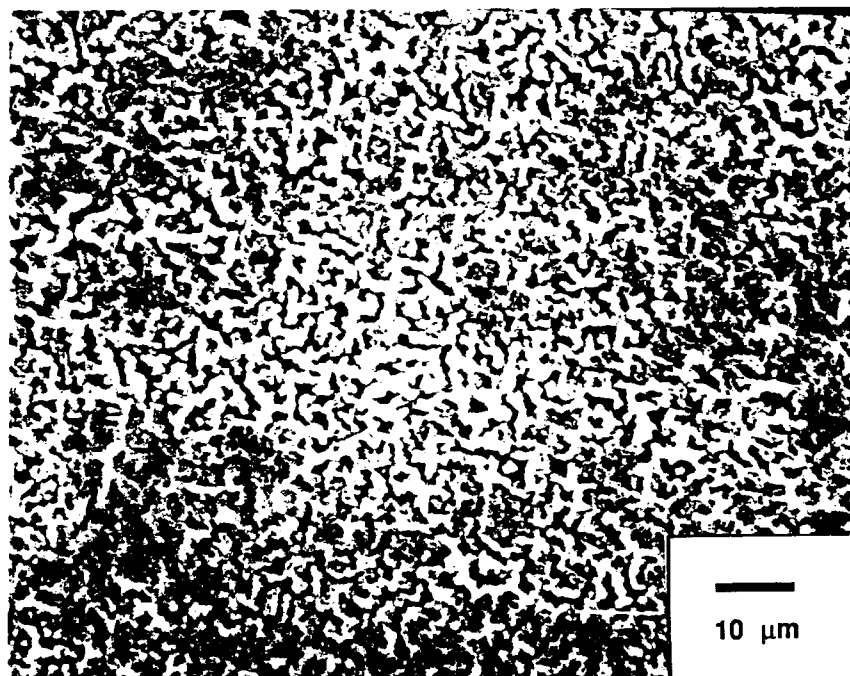MTS/H2 at 1300°C.

A

B

FIGURE 3. Run 52. SEM micrographs of film grown from 0.33% MTS/H2 at 1300°C.
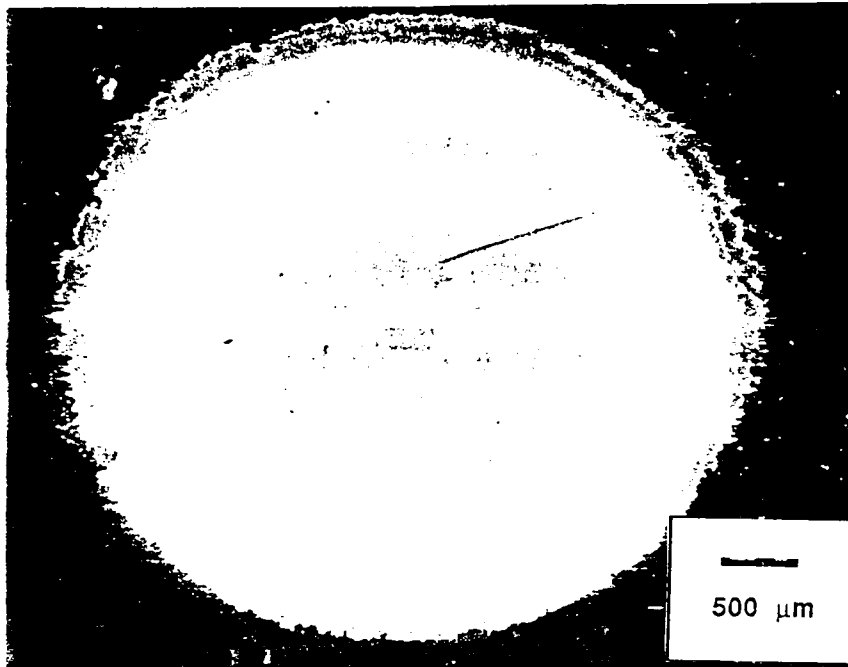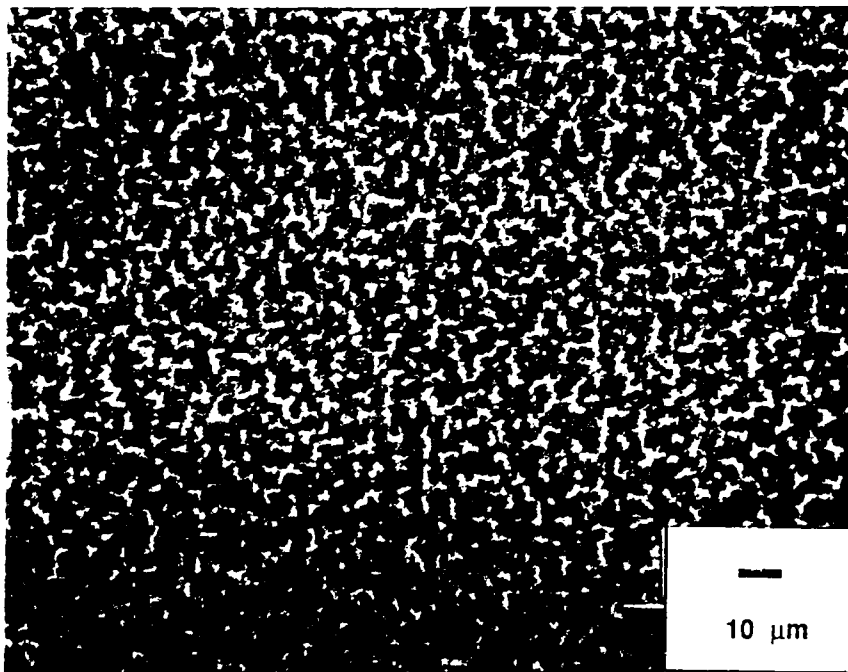
A

B

FIGURE 4. Run 53. SEM micrographs of film grown from 0.40% MTS/H2 at 1300°C.
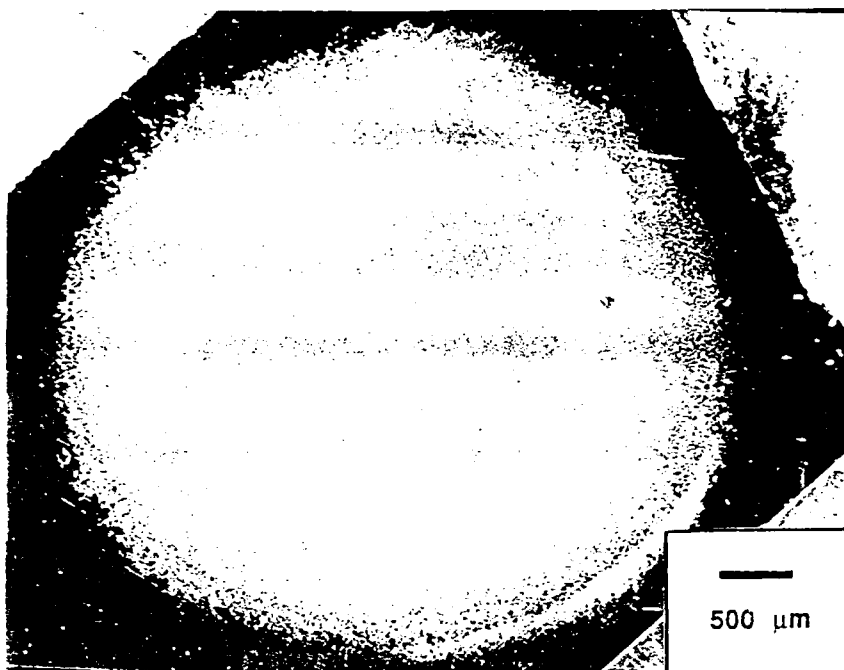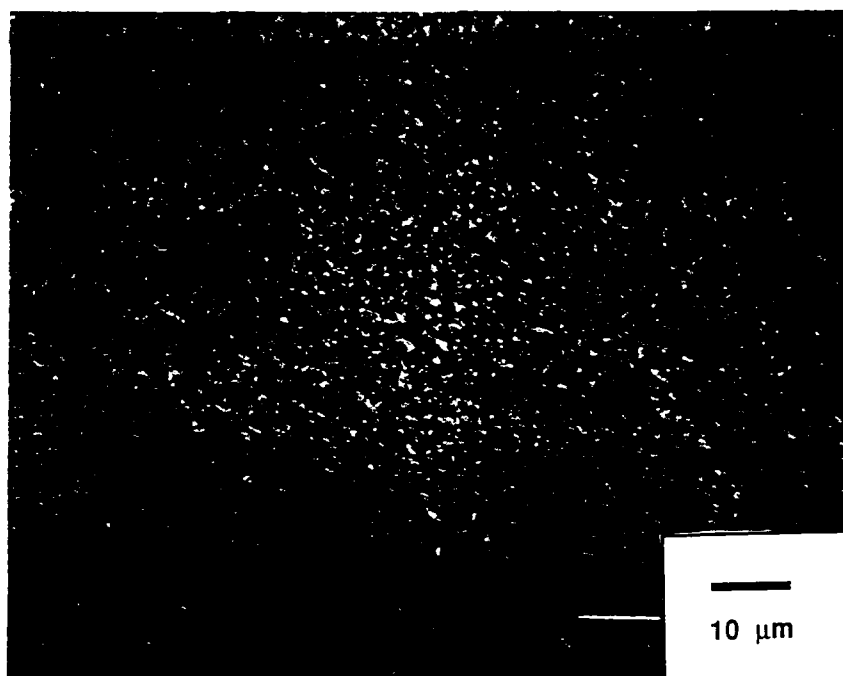
A

B

FIGURE 5. Run 59. SEM micrographs of film grown from 1.0%
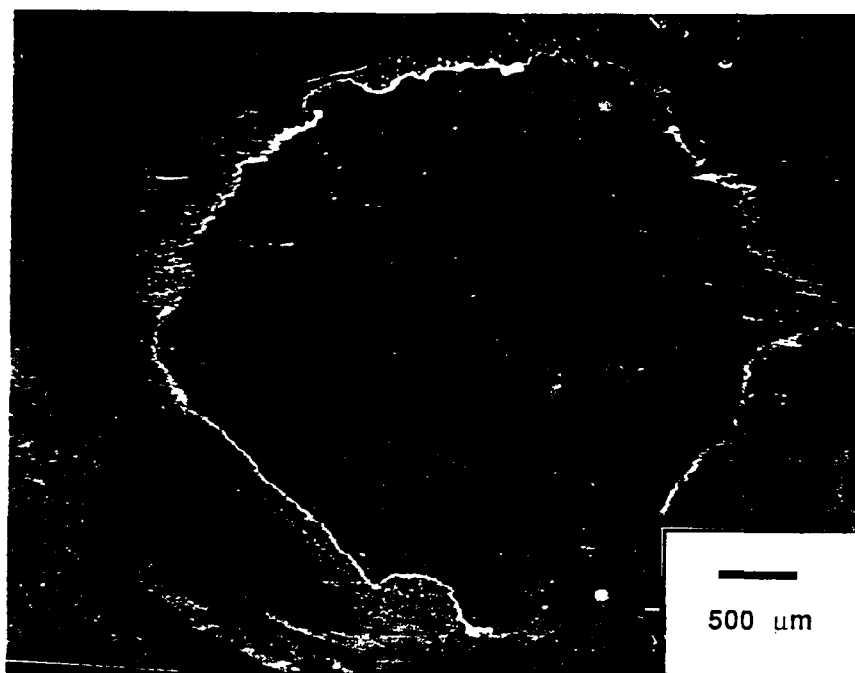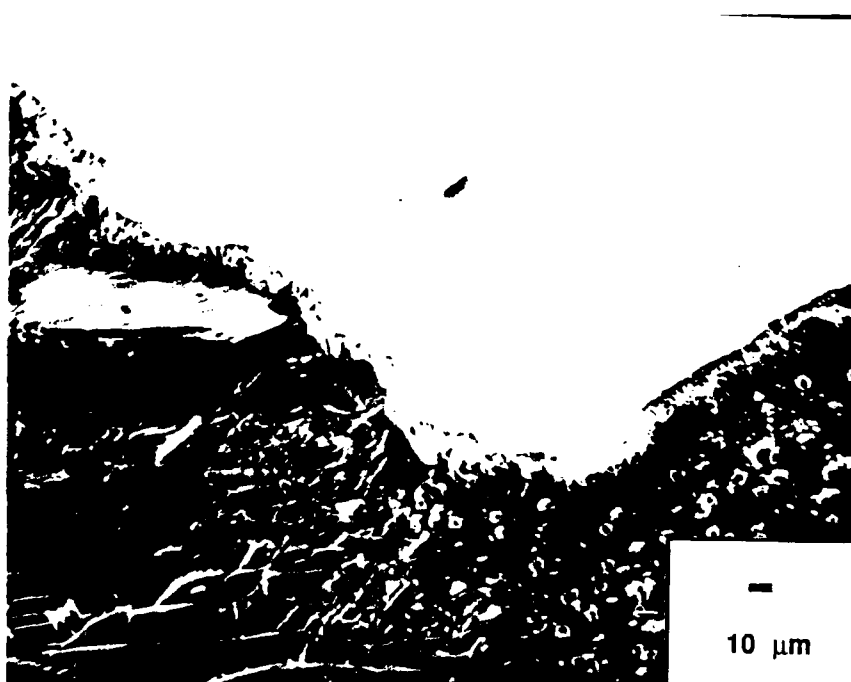MTS/H2 at 1300°C.

11

A

B

FIGURE 6. Run 60. SEM micrographs of film grown from 1.9%
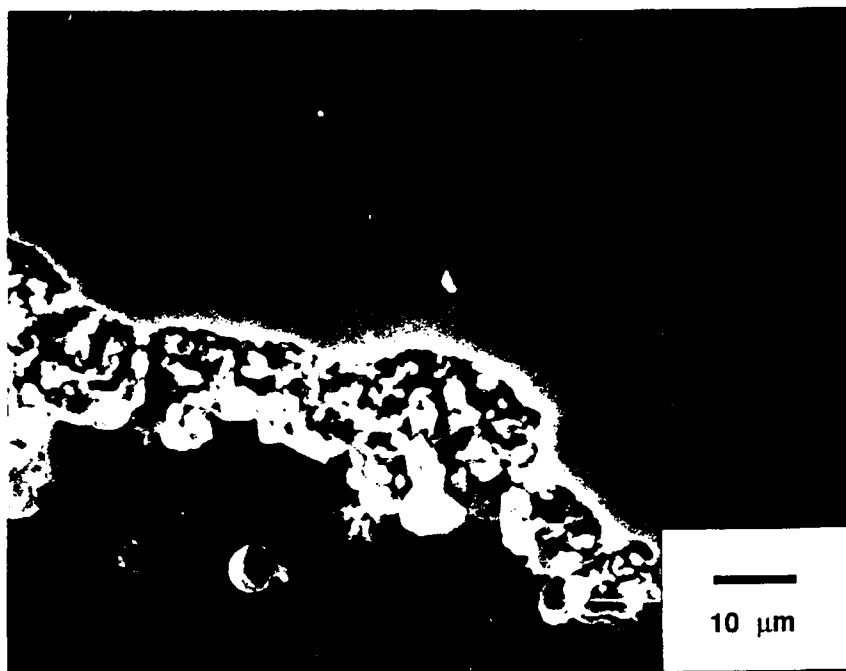MTS/H2 at 1300°C.

A

B

FIGURE 7. Run 63. Lower magnification SEM micrographs of film grown from 1.9% MTS/H2 at 1300 - 1400°C.

A

B

FIGURE 8. Run 63. Higher magnification SEM micrographs of film grown from 1.9% MTS/H2 at 1300 - 1400°C.

view, as in Figure 3B, these early crystals are oriented cubically, with 90° angles clearly seen in Figure 3B.

The best result so far was run 63. Unfortunately, the belljar viewport used by the optical pyrometer to measure Si surface temperture during a run was occluded during run 63. Since optical pyrometer measurements automatically determines the power output from the rf power supply, rf output was boosted to compensate for a perceived loss of substrate temperature. The boosted rf power increased the substrate temperature to near the melting point of silicon (1410°C); after removal from the reactor, the perimeter of the silicon substrate was found to be partially melted.

There is evidence that run 63 may have been DMI's first heteroepitaxial β-SiC film on silicon. The film was optically transparent, with a very smooth and flat texture. The film had a slight greenish color under the optical microscope. Figures 7 and 8 indicate that the film was run long enough for the numerous subgrains to coalesce into a continuous single crystal. The numerous subgrains had a thickness of 4-6 μm; the continuous smooth film atop the subgrains had a thickness under 1 μm. Under careful inspection of Figures 7B and 8B, *orange peel* surface texture is discernable. This microstructure reflects the transition of the SiC film from the etched surface at the bottom of the silicon crater to the smoother, orange peel surface at the top of the film.

The Raman spectrum of film 63 was weak in intensity. The spectrum of Figure 9 indicates the presence of both α-SiC and β-SiC. A TO mode of α-SiC is observed at 786 cm^{-1} and a TO mode of β-SiC is at 798 cm^{-1}. Despite total thicknes of the film being 5 - 7 μm, the weak Raman response is puzzling. The film may contain a high concentrations of crystallograpic defects which reduce Raman intensity. The multiple subgrains seen in Figure 8B support this defective crystal theory. In future growth runs, DMI will attempt to grow films at a slower rate in order to improve the morphology and increase the crystallinity of the β-SiC monocrystals.

3.0   FUTURE WORK

DMI will work to finish the statement of work as summarized in Section 1 of this Report. The immediate goal will be to grow one or more monocrystalline β-SiC films to a thickness at least 30 μm. The silicon wafer will then be selectively etched to create a freestanding β-SiC crystal.

DMI has installed a tube furnace with a fused silica liner. The furnace was installed with the necessary safety equipment to perform chlorinated thermal oxidation of silicon or silicon carbide. The exhaust from the furnace is plumbed with
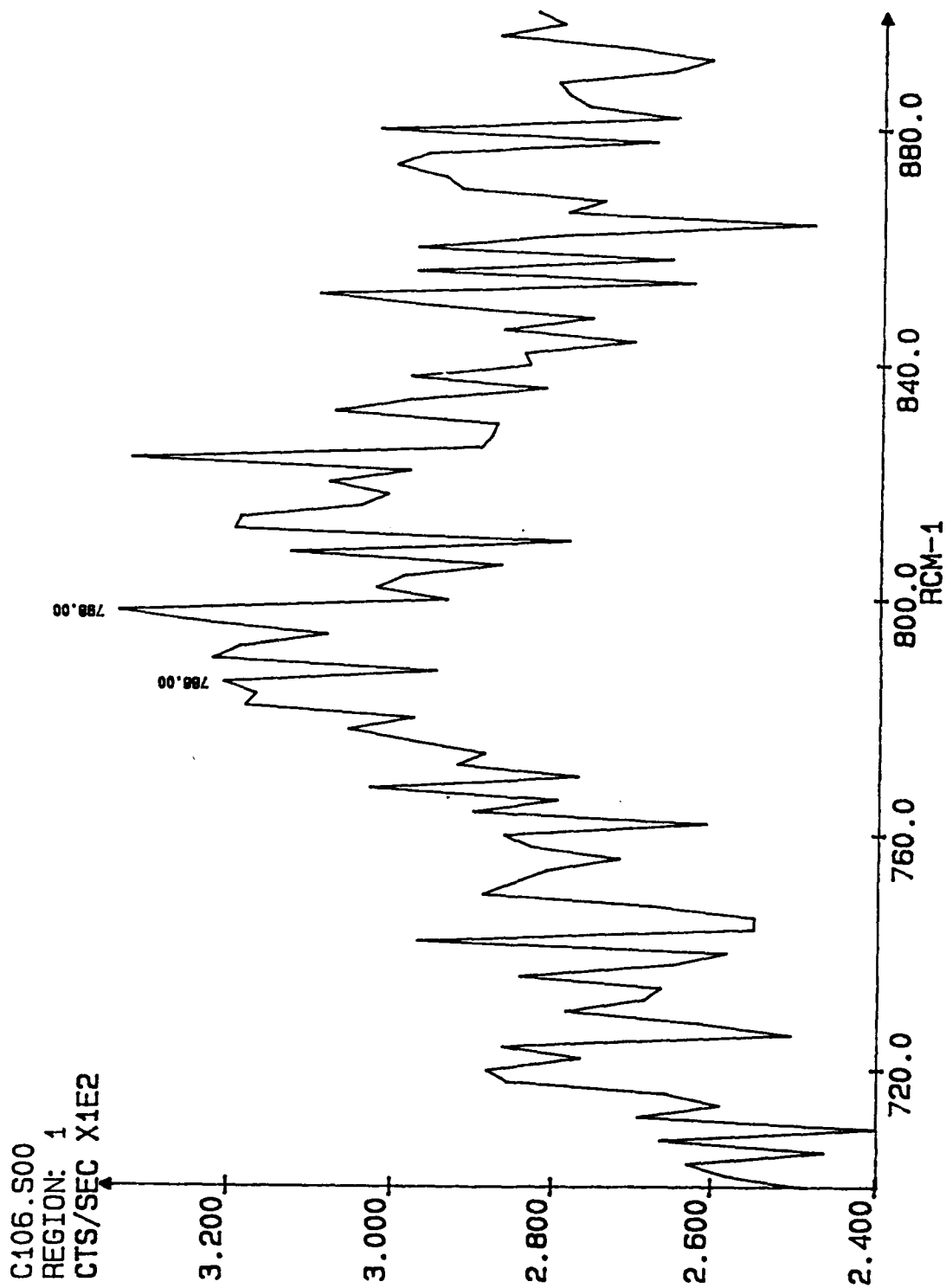
FIGURE 9. Raman spectrum of film grown by run 63. The TO mode of alpha silicon carbide is present at 786 cm-1 and the TO mode of beta silicon carbide is present at 798 cm-1.

Teflon tubing; a corrosion-resistant exhaust blower draws the effluent from the tube furnace into DMI's scrubber.

DMI will *not* use a traditional mixture of HCl gas plus O_2 to perform the chlorinated oxidation of β-SiC crystals. Instead, DMI will employ mixtures of trichloroethane (TCA) and O_2 using equipment supplied by J. C. Schumacher Co (JCS). DMI has a JCS *M-dot* bubbler filled with semiconductor-grade TCA. DMI will flow TCA/O_2 mixtures prescribed by JCS which can produce the same results as flowing between 1 to 10% HCl/H_2. TCA offers many safety advantages over HCl gas. TCA is a liquid which does not decompose into HCl until well inside the hot tube furnance; the TCA reacts with the O_2 to volatilize carbon as CO_2. Corrosion of the inlet tubing is minimized since TCA liquid or vapor is not very corrosive.